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(54) Method of improving scuff and cut resistance of ionomer covered game ball

(57) A game ball has an ionomeric cover 12 which comprises a combination of ionomeric crosslinks and covalent crosslinks. The game ball cover is superior in at least one of cut resistance and scuff resistance to a conventional cover that does not have covalent crosslinks but is otherwise substantially identical in composition. The game ball cover is particularly useful for improving the durability of golf balls to be struck with sharp-grooved clubs. The crosslinking may comprise radiation-induced crosslinking.

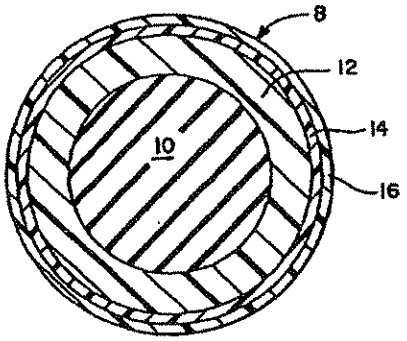

FIG. 1

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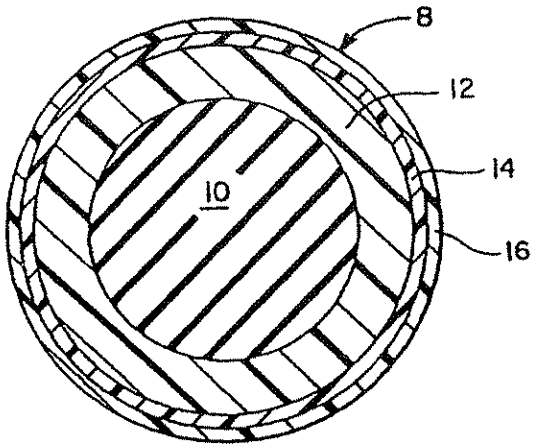

FIG. 1

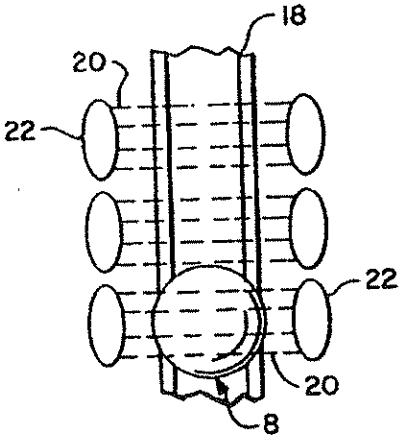

FIG. 2

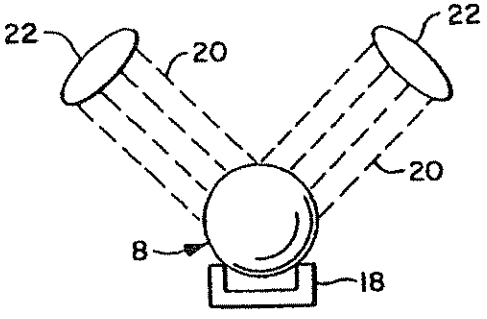

FIG. 3

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METHOD OF IMPROVING SCUFF AND CUT RESISTANCE OF IONOMER COVERED GAME BALL

This invention relates generally to balls, and more particularly to a game ball having an ionomeric cover, for example a golf ball.

Before the development of ionomers, balata was the preferred material for golf ball covers. Polyethylene also was proposed for use as a golf ball cover material but was generally deemed highly inferior to balata in imparting playability and durability characteristics to the ball, due to its brittleness and high hardness, and thus never became a commercially successful golf ball cover material.

Balata golf ball covers have now been replaced to a great extent by ionomeric cover materials. Ionomers may be copolymers of an olefin and an α, β-ethylenically unsaturated carboxylic acid with a portion of the carboxylic acid groups neutralized by a metal ion. The metal ions serve as crosslinking agents, because they are ionically bonded to carboxylic acid groups in adjacent copolymer chains. Instead of having thermally irreversible covalent bonding, ionomers have thermolabile crosslinking in which metal ions become part of the chemical structure of the ionomer upon

crosslinking, and these crosslinks are reversible. For purposes of the present application, this type of crosslinking is referred to as ionic crosslinking. One of the advantages of ionic crosslinking in golf ball materials is the ability of ionic bonds to re-form after breaking as a result of processing at elevated temperatures.

There are numerous advantages to the use of ionomers in making golf ball covers. On the other hand, one drawback of conventional golf balls with soft ionomeric covers is that the covers are prone to scuffing and cutting, particularly when hit with irons which have sharp grooves. It would be useful to develop a golf ball with a soft ionomeric cover which is highly resistant to cutting and scuffing by sharp-grooved clubs.

Some examples of the present invention are mentioned below.

One object of the invention is to provide an ionomeric game ball cover having improved scuff resistance and/or cut resistance.

Another object of the invention is to provide a method for imparting improved scuff resistance and/or cut resistance to a game ball cover.

Yet another object of the invention is to provide a golf ball with a soft cover which is well suited for use with golf club irons having sharp grooves.

Yet another object of the invention is to provide a method of forming a golf ball with a soft cover which has excellent scuff resistance and/or cut resistance.

A first aspect of the present invention provides a ball, comprising:

a cover comprising at least one ionomer resin that comprises copolymer of olefin and α, ß-ethylenically unsaturated carboxylic acid that is sufficiently neutralized with metal ions so as to have a sufficient degree of covalent crosslinking to impart to the cover an increased resistance to at least one of scuffing and cutting.

In said first aspect of the invention, said ball may be a game ball, for example, a golf ball. Said cover may have a dimpled surface. Said degree of covalent crosslinking may be sufficient to impart to the cover a Shore D hardness at most 10% greater than the Shore D hardness of a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking. Said

degree of covalent crosslinking may be sufficient to impart to the cover a Shore D hardness at most 5.0% greater than the Shore D hardness of a cover having a substantially identical composition but which does not have a substantial degree of said covalent crosslinking. Said degree of covalent crosslinking may be sufficient to impart to the ball a PGA compression at least 5% harder than the PGA compression of a ball with a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking. Said degree of covalent crosslinking may be sufficient to impart to the ball a coefficient of restitution at least 0.50% greater than a coefficient of restitution of a ball with a cover having a substantially identical composition but which does not have radiation-induced covalent crosslinking. Said copolymer may have radiation-induced covalent crosslinking to increase the resistance of the cover to at least one of scuffing and cutting. Said radiation-induced covalent crosslinking may be provided by irradiating the cover by a method comprising utilising an electron beam. Said irradiation may comprise electron beam dosage of at least 1 megarads.

Said irradiation may be before and/or after application of coating over the cover. After said

irradiation, a top coating may be applied to the irradiated cover. Said copolymer may further comprise acrylate. Said neutralization of said carboxylic acid may correspond to 10 to 100% neutralization with said metal ions. Said cover may have a Shore D hardness of at most 65.

A second aspect of the present invention provides a method of forming a ball of said first aspect of the present invention.

The invention in one preferred form is a game ball having a cover comprising an ionomer resin. The ionomer resin may comprise a copolymer of an olefin and an α, ß-ethylenically unsaturated carboxylic acid which is 10-100% neutralized with metal ions. The copolymer has a sufficient degree of covalent crosslinking to impart to the cover improved resistance to at least one of scuffing and cutting. In a particularly preferred form of the invention, the game ball is a golf ball. Preferably, the game ball has a dimpled surface. The covalent crosslinking preferably comprises irradiation-induced covalent crosslinking.

In another form of the invention, the degree of covalent crosslinking is appropriate to impart to the cover a Shore D hardness which is no more than 10% greater, and more preferably no more than 5% greater,

than the Shore D hardness of a cover having an identical composition but which does not comprise a substantial degree of covalent crosslinking. Preferably, the copolymer further comprises acrylate.

Another aspect of the invention is a method of forming a game ball having a cover comprising an ionomer, said method comprising irradiating the ionomer in the cover under conditions appropriate to covalently crosslink the ionomer in order to increase the resistance of the cover to at least one of scuffing and cutting without substantially impairing other playability characteristics of the ball.

In a particularly preferred form of the invention, the game ball is a golf ball. Preferably, the game ball has a dimpled surface.

In one preferred form of said method of the invention, a game ball is subjected to irradiation comprising electron beam treatment at a dosage of at least 1 megarads. The game ball cover preferably is irradiated prior to application of a top coat over a cover. The method of the invention preferably further comprisesthe step of applying a top coat over the cover before or after irradiation.

The present invention is exemplified by the following detailed disclosure with reference to the

accompanying drawings wherein:

Fig. 1 shows one example of a golf ball according to the present invention.

Figs. 2 and 3 schematically show one example for practicing the method of the present invention.

The game balls of the present invention are surprisingly superior in their scuff (abrasion) resistance and cut resistance to conventional game balls which have not been electron beam treated, and which contain similar quantities of ionomer and have a similar hardness. Furthermore, the golf balls and other game balls of the invention are comparable in scuff and cut resistance to game balls having non-ionomeric compositions, such as polyurethanes, with similar properties of compression, coefficient of restitution (COR), and hardness.

The game balls of the present invention may be formed by first obtaining an uncoated or coated game ball having an ionomeric cover. An "uncoated" game ball as the term is used in this application is a one, two, or multi-piece game ball to which no primer or top coat has been applied over the ionomeric cover. In contrast, a "coated" game ball as this term is used in this application is a ball which has a primer coat and/or a top coat over the ionomeric cover layer. The coated or

uncoated game ball of the invention may be subjected to irradiation under conditions appropriate to induce covalent crosslinking of the ionomer. This type of direct covalent bonding has been found to take place in ionomeric cover materials when electron beam treatment is applied at a dosage of 2 or more megarads and is expected to also be useful at lower dosages, for example, 1 megarad.

For clarity of description and ease of understanding, the invention will be described in connection with golf balls although it will be understood that other game balls, for example softballs, basketballs, baseballs, soccer balls, vollyballs, street hockey balls, footballs, etc. can advantageously employ the features of the present invention.

Referring now to the drawings, and in particular to Fig. 1, one example of a golf ball according to the present invention is shown and is designated as 8. The ball has a core 10, which is solid, or is formed from any other suitable type of core composition. An ionomeric cover 12 surrounds the core 10. A thin primer coat 14 is applied to the outer surface of cover 12. A thin top coat 16 surrounds the primer coat 14. The thicknesses of primer coat 14 and top coat 16 are exaggeratedfor illustrative purposes.

In accordance with the present invention, after the cover layer 12 is applied over the core, the cover layer 12 is subjected to irradiation at a dose of about 1 or more megarads in order to covalently crosslink the ionomeric cover material. Particularly good results are obtained when the dosage is in the range of 2 - 12 megarads. In a most preferred form of the invenion, a dosage in the range of 4 - 8 megarads is utilized. AS used herein, the term "irradiation" may refer to short-duration irradiation using an electron beam or the like, rather than to mere exposure to sunlight, which would result in a dosage of well below 1 megarad. Irradiation takes place at a temperature below the melting or deformation temperature of the cover layer, and for convenience preferably takes place at ambient temperature.

The cover 12 can be irradiated prior to or after application of primer coat 14 and top coat 16. Furthermore, primer coat 14 can be eliminated if adhesion of top coat 16 to cover 12 is sufficient to render the ball suitable for competitive play, as is commonly the case with softballs and baseballs, and may also be the case for other game balls.

The game ball of the invention can be irradiated with electrons, neutrons, protons, gamma

rays, x-rays, helium nuclei, etc. In a particularly preferred form of the invention, the scuff and cut resistance of cover 12 is enhanced by subjecting the cover to electron beam treatment at a dosage suffficient to significantly improve scuff resistance and COR without excessively hardening the compression. The game ball preferably obtains an improvement in COR of at least 0.5% as a result of irradiation of the cover.

The cover composition contains high quantities of ionomer. Thus, the irradiated cover material may have a combination of ionic crosslinks and covalent crosslinks. Particularly preferred ionomers or ionomer blends comprise ionic copolymers containing an olefin, an unsaturated carboxylic acid, and an acrylate. Such polymers may have a Shore D hardness in the range of 20 - 60. Non ionomeric materials can be blended with the ionomer as long as an acceptable increase in scuff resistance and/or cut resistance is obained as a result of covalent crosslinking of the ionomer. Some non-limiting examples of materials to be blended with an ionomer are ethylene-ethyl acrylate; ethylene-methyl acrylate; ethylene-vinyl acetate; low density polyethylene; linear low density polyethylene; metallocene catalyzed polyolefins such as ENGAGE polyolefins available from Dow Chemical and EXACT

polyolefins available from Exxon; non-ionomeric acid copolymers such as PRIMACOR available from Dow Chemical, and NUCREL available from Du Pont; and a variety of thermoplastic elastomers, e.g. KRATON available from Shell, SANTOPRENE available from Monsanto, and HYTREL, available from Du Pont, etc.

If the game ball cover is irradiated prior to application of a primer coat 14 and/or top coat 16, there is no particular restriction on the type of primer coat and/or top coat to be used. If irradiation occurs afer application of a primer coat and/or a top coat over the cover 12, it is important to ensure that the radiation will penetrate the coating, and that the dosage of radiation is sufficient to covalently crosslink the cover material without adversely affecting the properties of the primer and/or top coat to a substantial degree. Due to the thinness of the primer coat and top coat on most game balls, for example golf balls, it has been found that little change in radiation dosage is required if irradiation occurs after application of such coatings.

Golf balls according to the invention preferably have a post-irradiation PGA compression of in the range of 10 - 110. In a particularly preferred form of the invention,the golf balls have a PGA compression

of in the range of 40 - 100 after irradiation. It has been found that excellent results are obtained when the post-irradiation PGA compression of the golf balls is in the range of 60 - 100. The irradiation preferably results in an increase in PGA compression of at least 5% compared to the PGA compression of the ball prior to treatment. The coefficient of restitution of the golf balls of the invention after treatment may be in the range of .780 or greater. Preferably, the COR of the golf balls is in the range of .790 - .830 and most preferably in the range of .800 - .830. The Shore D hardness of the golf balls of the invention after irradiation may be in the range of 40 - 80. Particularly goods results are obtained when the Shore D hardness of the golf balls is in the range of 50 - 70, and most preferably in the range of 50 - 60.

The invention is particularly well suited for use in making dimpled, pebbled, and other game balls which do not have a smooth outer surface, for example game balls with simulated stitching. A smooth ball is less susceptible to scuffing than a dimpled ball since dimples give the golf club groove a sharp-edged surface to "catch." Pebbles clearly are susceptible to shearing when dribbled on a hard surface, or the like. Likewise on a molded-cover softball, the stitching is a raised

area that will be sheared or compressed more than the smooth-surfaced area by a bat and/or by the turf, dirt, etc.

One example of a method for electron beam treating golf balls according to the invention is described in connection with Figs. 2 and 3. The golf ball 8 is placed on a channel 18 along which it slowly moves. Electrons 20 from electron beam lamps 22 contact the surface of the ball 8. The lamps are positioned to provide a generally uniform dose of radiation on the entire surface of the ball as the ball rolls along the channel 18. Preferably, the balls are irradiated with an electron beam dosage of 1 or more megarads, more preferably in the range of 2 - 12 megarads. The intensity of the dosage preferably is in the range of 1 - 20 MeV.

The golf balls of the invention are found to exhibit a post-treatment scuff resistance in the range of 1 - 3 on a scale of 1 - 4. It is preferred that the treatment be appropriate to provide the golf balls with a scuff resistance in the range of 1 - 2.5, and more preferably in the range of 1 - 2. Golf balls according to the invention may have a cut resistance in the range of 1 - 3 on a scale of 1 - 5. It is preferred that the golf balls of the invention have a cut resistance in the range of 1 -2.5 and most preferably in the range of 1-2.

The scuff resistance test was conducted in the following manner:

a Top-Flite pitching wedge (1994) with box grooves was obtained and was mounted in a Miyamae driving machine. The club face was oriented for a square hit. The forward/backward tee position was adjusted so that the tee was 10.16 cm (four inches) behind the point in the downswing where the club was vertical. The height of the tee and the toe-heel position of the club relative to the tee were adjusted in order that the center of the impact mark was 1.905 cm (3/4 of an inch) above the sole and was centered toe to heel across the face. The machine was operated at a clubhead speed of 38.1 meters per second (125 feet per second). Three samples of each ball were tested. Each ball was hit three times. After testing, the balls were rated according to the following table:

Rating	Type of damage
1	Little or no damage (groove markings or dents)
2	Small cuts and/or ripples in cover
3	Moderate amount of material lifted from ball surface but still attached to ball

4 Material removed or barely attached

Cut resistance was measured in accordance with the following procedure: a golf ball was fired at 41.148 meters per second (135 feet per second) against the leading edge of a 1994 Top-Flite Tour pitching wedge, wherein the leading edge radius is 0.079 cm (1/32 inch), the loft angle is 51 degrees, the sole radius is 6.35 cm (2.5 inches), and the bounce angle is 7 degrees.

The cut resistance of the balls tested herein was evaluated on a scale of 1 -5. A 5 represents a cut that extends completely through the cover to the core; a 4 represents a cut that does not extend completely through the cover but that does break the surface; a 3 does not break the surface of the cover but does leave a permanent dent; a 2 leaves only a slight crease which is permanent but not as severe as 3; and a 1 represents virtually no visible indentation or damage of any sort.

It has been found that golf balls which are treated according to the irradiation technique of the present invention exhibit a particular improvement in scuff and/or cut resistance. This improvement is particularly significant when the golf balls are struck with a square-grooved iron. It has been found that square-grooved irons and other sharp-grooved irons tend

to abrade and damage golf ball covers more readily than irons having "V-type" grooves.

Having generally described the invention, the following detailed examples are included for purposes of illustration so that the invention may be more readily understood and are in no way intended to limit the scope of the invention unless otherwise specifically indicated.

Example 1

Polybutadiene golf ball cores having an average coefficient of restitution (COR) of .790 and a PGA compression of 90 were obtained. The cores were covered with a relatively soft, 0.1397 cm (0.055 inch) thick cover formed from an ionomeric composition, designated as ionomer 1, which comprises a blend of a hard sodium ionomer and a soft zinc ionomer. Pigments and an optical brightener were also included in the cover composition. The hard ionomer is a copolymer containing two monomer types, namely an α-olefin and an acrylic-type carboxylic acid. The soft ionomer is a copolymer which contains three types of monomers, namely an α-olefin, an acrylic-type carboxylic acid, and an acrylate. The cover was formed over the core. The balls were primed with a polyurethane-based primer with a thickness of 0.0127 cm (0.5 thousandths of an inch) and coated with a polyurethane top coat with a thickness of 0.0127 cm (0.5 thousandths of an inch). The properties of these balls prior to electron beam treatment are shown in Table 1.

A portion of the balls were subjected to electron beam treatment at dosages of 2,4,6,8, and 11 megarads at an energy level of 10 MeV. Changes in the properties of the balls are shown in Table 1.

As indicated in Table 1, the scuff resistance of the golf balls substantially improved in the range of electron beam dosages of 2 to 6 megarads. The cut resistance of the balls improved in the range of electron beam dosages of 6 to 8 megarads. Meanwhile, the change in Shore D hardness in the dosage range of 2 to 8 was only 1.

TABLE 1

Cover Material	Dosage (Megarads)	Weight	PGA Comp	COR	Shore D	Scuff Resistance	Cut Resistance
Ionomer Blend 1 (coated prior to treatment)	2.0	45.6	93	.788	54	2.5	2 - 3
	4.0	45.6	97	.797	55	1-2	2 - 3
	6.0	45.6	98	.795	55	1.5	2 - 3
	8.0	45.6	98	.797	55	1.5	2
	11.0	45.6	101	.802	65	1.5	2
	0	45.6	92	.787	54	3.5	3
Ionomer Blend 2 (uncoated)	2.0	45.4	96	.822	63	--	--
	4.0	45.4	97	.822	63	--	--
	0	45.4	88	.812	62	--	--
Ionomer Blend 2 (coated with primer and top coat prior to treatment)	6.0	45.6	101	.829	64	1.5	1 - 2
	8.0	45.5	103	.828	64	1.5	1 - 2
	0	45.6	88	.813	63	2.0	1 - 2

(Weight = Ball weight, grams)

Example 2

Golf ball cores having an average PGA compression of 85 and an average COR of .800 were obtained. The cores were covered with a hard zinc-sodium ionomeric composition containing two monomer types, namely an α-olefin and a carboxylic acid. The initial properties of the covered cores prior to priming and finish coating are shown in Table 1.

A portion of the golf balls were painted with the same polyurethane-based primer as was used in Example 1 and then coated with the same polyurethane top coat as was used in Example 1. Subsequently, a portion of both the unprimed and unfinished golf balls and the primed and finished golf balls were subjected to electron beam treatment in the dosages shown in Table 1. Properties of compression, COR, Shore D hardness and scuff resistance are shown in Table 1.

As indicated in Table 1, the scuff resistance of the finished golf balls increased substantially while resulting in a minimal increase in Shore D hardness.

In this specification(description, claims and abstract), precise values include values about or substantially the same as precise values, e.g. 10% includes values about or substantially the same as 10%.

Imperial values include their metric values. The present disclosures include the whole of the description, the appended claims, the appended drawings, and the appended abstract; and modifications or equivalents thereof.

As will be apparent to persons skilled in the art, various modifications and adaptations of the structure above described will become readily apparent without departure from the spirit and scope of the invention, the scope of which is defined in the appended claims.

CLAIMS

1. A ball, comprising:

a cover comprising at least one ionomer resin that comprises copolymer of olefin and α,β-ethylenically unsaturated carboxylic acid that is sufficiently neutralized with metal ions so as to have sufficient degree of covalent crosslinking to impart to the cover an increased resistance to at least one of scuffing and cutting.

2. A ball as claimed in claim 1, wherein the ball is a game ball.

3. A ball as claimed in claim 2, wherein the game ball is a golf ball.

4. A ball as claimed in any one of claims 1 to 3, wherein the cover has a dimpled surface.

5. A ball as claimed in any one of claims 1 to 4, wherein said degree of covalent crosslinking is sufficient to impart to the cover a Shore D hardness at most 10% greater than the Shore D hardness of a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking.

6. A ball as claimed in any one of claims 1 to 5, wherein said degree of covalent crosslinking is sufficient to impart to the cover a Shore D hardness at most 5.0% greater than the Shore D hardness of a cover having a substantially identical composition but which does not have a substantial degree of said covalent crosslinking.

7. A ball as claimed in any one of claims 1 to 6, wherein the degree of covalent crosslinking is sufficient to impart to the ball a PGA compression at least 5% harder than the PGA compression of a ball with a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking.

8. A ball as claimed in any one of claims 1 to 7, wherein said degree of covalent crosslinking is sufficient to impart to the ball a coefficient of restitution at least 0.50% greater than a coefficient of restitution of a ball with a cover having a substantially identical composition but which does not have radiation-induced covalent crosslinking.

9. A ball as claimed in any one of claims 1 to 8, wherein said copolymer has radiation-induced covalent crosslinking to increase the resistance of the cover to at least one of scuffing and cutting.

10. A ball as claimed in claim 9, wherein said radiation-induced covalent crosslinking has been provided by irradiating the cover by a method comprising utilising an electron beam.

11. A ball as claimed in claim 10, wherein said irradiation is at least 1 megarads.

12. A ball as claimed in claim 11, wherein said irradiation is at least 2 megarads.

13. A ball as claimed in 12, wherein said irradiation is in the range 2 to 12 megarads.

14. A ball as claimed in claim 13, wherein said irradiation is in the range 2 to 6 megarads.

15. A ball as claimed in claim 13, wherein said irradiation is in the range 4 to 8 megarads.

16. A ball as claimed in claim 13, wherein said irradiation is in the range 6 to 8 megarads.

17. A ball as claimed in any one of claims 9 to 16, wherein the irradiation has an intensity in the range of 1 to 20 MeV.

18. A ball as claimed in any one of claims 9 to 17, wherein said irradiation was applied before and / or after application of at least one coating over the cover.

19. A ball as claimed in any one of claims 9 to 18, wherein after said irradiation top coating was applied to the irradiation cover.

20. A ball as claimed in any one of claims 1 to 19, wherein said copolymer further comprises acrylate.

21. A ball as claimed in any one of claims 1 to 20, wherein said neutralization of said carboxylic acid corresponds to 10 to 100% neutralization with said metal ions.

22. A ball as claimed in any one of claims 1 to 21, wherein the cover has a Shore D hardness of at most 65.

23. A ball as claimed in claim 1, substantially as hereinbefore described with reference to the accompanying drawings.

24. A ball as claimed in claim 1, substantially as described in the Examples.

25. A game ball having a cover comprising an ionomer resin, the ionomer resin comprising copolymer of olefin and α, β-ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized with metal ions, the copolymer having a sufficient degree of covalent crosslinking to impart to the cover improved resistance to at least one of scuffing and cutting.

26. A game ball according to claim 25, wherein the game ball is a golf ball.

27. A game ball according to claim 25, wherein the cover has a dimpled surface.

28. A game ball according to claim 25, wherein the covalent crosslinking comprises radiation-induced covalent crosslinking.

29. A game ball according to claim 25, wherein the degree of covalent crosslinking is appropriate to impart to the cover a Shore D hardness which is no more than 10% greater than the Shore D hardness of a cover having a substantially identical composition but which does not include a substantial degree of covalent crosslinking.

30. A game ball according to claim 25, wherein the copolymer furher comprises an acrylate.

31. A game ball according to claim 25, wherein the cover has a Shore D hardness of 65 or less.

32. A game ball according to claim 28, wherein the degree of covalent crosslinking is sufficien to impart to the ball a coefficient of restitution which is at least 0.50% greater than a coefficient of restitution of a ball with a cover having a substantially identical composition but which does not have radiation-induced covalent crosslinking.

33. A game ball according to claim 26, wherein the degree of covalent crosslinking is sufficient to impart to the ball a PGA compression which is at least 5% harder than the PGA compression of a golf ball with a cover having a substantially identical composition but which does not have a substantial degree of covalent crosslinking.

34. A game ball having a cover comprising ionomer resin, the ionomer resin comprising copolymer of α-olefin, acrylate, and α,β-ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized with metal ions, the copolymer having a degree of radiation induced covalent crosslinking which is sufficient to substantially improve the resistance of the cover to a least one of scuffing and cutting while resulting in a cover hardness (Shore D) which is no more

than 5.0% higher than the Shore D hardness of a cover which is substantially identical in composition but does not contain covalent crosslinking.

35. A game ball according to claim 34, wherein the game ball is a golf ball.

36. A game ball according to claim 34, wherein the cover has a dimpled surface.

37. A method of forming a ball optionally a game ball, comprising:
obtaining a game ball having a cover comprising an ionomer;
and
irradiating the ionomer in the cover under conditions appropriate to covalently crosslink the ionomer in order to increase the resistance of the cover to at least one of scuffing and cutting without substantially impairing other playability characteristics of the ball.

38. A method according to claim 37, wherein the game ball is a golf ball.

39. A method according to claim 37, wherein the game ball has a dimpled surface.

40. A method according to claim 37, wherein the cover is irradiated using an electron beam.

41. A method according to claim 40, wherein the cover is subjected to electron beam treatment at a dosage of at least 2 megarads.

42. A method according to claim 37, wherein the game ball cover is irradiated after application of a coating over the cover.

43. A method according to claim 37, comprising the step of applying a top coating over the cover after irradiation.

44. A method according to claim 37, wherein the ionomer comprises copolymer of α-olefin, acrylate, and α,β-ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized with metal ions.

45. A method of forming a game ball, comprising:
obtaining an unfinished game ball having a cover comprising an ionomer;
forming a coating over the cover; and
irradiating the ionomer in the cover at a dosage of at

least 2 megarads to covalently crosslink the ionomer to a degree sufficient to increase at least one of the scuff resistance and cut resistance of the cover without reducing the coefficient of restitution of the cover.

46. A method according to claim 45, wherein the game ball is a golf ball.

47. A method according to claim 45, wherein the game ball has a dimpled surface.

48. A method according to claim 45, wherein the ionomer comprises copolymer of α-olefin, acrylate, and α,β-ethylenically unsaturated carboxylic acid which is 10 - 100% neutralized with metal ions.

49. A method of forming a golf ball according to claim 1, said method being substantially as hereinbefore described with reference to the accompanying drawings.

50. A method of forming a golf ball according to claim 1, substantially as described in the Examples.

The Patent Office

30.

Application No: GB 9702144.8 **Examiner:** Alan Kerry
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Category	Identity of document and relevant passage	Relevant to claims
X	WPI Abstract Accession Number 88-060404/09 & JP 63 015832	1-3, 25, 37 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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(54) **Two-piece golf ball**

Zweiteiliger Golfball

Balle de golf en deux pièces

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Description

The present invention relates to a two-piece golf ball and, in particular, to a two-piece golf ball with an excellent shot feel.

Two-piece golf balls are widely used because of their excellent flight performance. However, they have some drawbacks, for example, the shot feel is harder than thread-wound golf balls and, particularly, when a bad shot is made, it gives an even harder feeling and therefore the advent of a two-piece golf ball with a good shot feel has been desired.

Various efforts have been made to bring the shot feel of the two-piece golf ball closer to that of the thread-wound golf ball. For example, the core of a two-piece golf ball has been made more flexible to reduce the hardness of the entire ball and thereby improve the shot feel (see Japanese Kokai Publication 63(1988)-220889). However, when the golf ball obtained by this method is hit, it feels heavy although it is more flexible and its shot feel is not necessarily similar to the shot feel of the thread-wound golf ball. When viewed from hardness distribution and compression strength, its impact force is large and the shot feel is not good enough.

The present invention provides a two-piece golf ball having a shot feel closer to that of a thread-wound golf ball, which is obtained by controlling the characteristics of the core and the thickness of the cover.

We have now discovered that by making the hardness distribution of the core more rigid at the outside and softer at the inside, adjusting the compression strength of the core, reducing the thickness of the cover to 1.5 to 2.1 mm (which is normally 2.1 to 2.4 mm) and optimizing these factors, it is possible to obtain a two-piece golf ball having a cover without a hard shot feel and a core with a light shot feel and appropriate flexibility, the ball as a whole being soft and light, having a better carry than conventional balls, without excessively reducing its hardness (expressed as PGA).

Accordingly, the present invention provides a two-piece golf ball comprising a core formed from a rubber composition comprising a base rubber, a co-crosslinking agent and an organic peroxide, and a cover covering the core, wherein the core has the following hardness distribution when measured by a JIS-C hardness meter;

(1) hardness at the center;	58 to 73
(2) hardness at 5 to 10 mm from the center;	68 to 78
(3) hardness at 15 mm from the center:	76 to 88
(4) surface hardness;	78 to 88

(in the hardness distribution, hardness (2) is substantially constant being within the above range, of which the tolerance is within ± 3 and the other values satisfy the relation of (1) < (2) < (3) ≦ (4)), the compression deformation of the core is in the range of from 2.8 to 3.5 mm when pressurized by an initial load of 10 kg up to a final load of 130 kg and the cover has a thickness of 1.5 to 2.1 mm.

The base rubber used in the present invention may be a natural and/or synthetic rubber which has been conventionally used for a two-piece core. In particular, cis-1,4-polybutadiene rubber containing at least more than 40% of the cis structure is preferred. If desired, natural rubber, polyisoprene rubber, styrene rubber, EPDM etc. may be blended into the polybutadiene rubber in appropriate amounts.

The co-crosslinking agent is not particularly restricted but, for example, a metal salt of an unsaturated carboxylic acid, in particular, a monavalent or divalent metal salt of an unsaturated carboxylic acid having 3 to 8 carbon atoms (for example, acrylic acid, methacrylic acid etc.) may be used. Zinc diacrylate is particularly preferred. The amount of the co-crosslinking agent is 20 to 35 wt parts, preferably 25 to 32 wt parts based on 100 wt parts of the base rubber. If the amount is less than 20 wt parts, the hardness of the ball is insufficient and the ball has a heavy and inferior shot feel and the durability is also inferior. When the amount exceeds 35 wt parts, the ball is too hard and the shot feel is also inferior.

The organic peroxide may be dicumyl peroxide or di-t-butylperoxide, but dicumyl peroxide is particularly preferred. The amount of the organic acid is from 0.5 to 5.0 wt parts, preferably 1.0 to 3.0 wt parts based on 100 wt parts of the base rubber. If it is less than 0.5 wt parts, the hardness of the ball is insufficient and the shot feel of the ball is heavy and inferior, while if it exceeds 5.0 wt parts, the ball is too hard and the shot feel is inferior.

The rubber composition used for the golf ball of the present invention may contain such additives as fillers, antioxidants, etc. if necessary. The filler generally used may be zinc oxide, barium sulfate etc. and the amount in the composition depends on the specific weight, size etc. of the cover and the core and is not particularly restricted, but it is usually from 10 to 40 wt parts based on 100 parts of the base rubber.

The core for the two-piece golf ball is formed by kneading the rubber composition sufficiently and curing it in a mold. The kneading conditions and curing conditions are well known to the industry but, usually curing is conducted at a temperature of from 140 to 180°C for 15 to 55 minutes.

The core of the golf ball of the present invention has such a hardness distribution when measured by a JIS-C hardness meter that it satisfies the conditions of (1) 58 to 73 at the center, (2) 68 to 78 at 5 - 10 mm from the center, (3) 76 to 88 at 15 mm from the center and (4) 78 to 88 at the surface. Particularly, the hardness (2) should be substantially

constant of which the tolerance is less than ± 3. The hardness values also satisfy the relation of (1) < (2) < (3) ≦ (4). The technology to specifically control the hardness distribution as above is described in Japanese Kokai Publication Sho 60(1985)-90575.

When the hardness is outside the aforesaid ranges, the durability decreases and the ball is exceedingly flexible and gives a heavy shot feel. When the hardness is higher than the above range, the impact force at the time of hitting is too large and the shot feel is inferior. When the hardness distribution is such that the hardness is higher as it is closer to the core surface, the impact force is larger than that described in the present invention, the softness of the shot feel is inferior, whilst in the case of a hardness distribution having a flat section as in the present invention, the impact force is small, a ball with a soft shot feel is obtained and the durability is also good.

Also it is necessary that the compression deformation of the core is in the range of from 2.8 to 3.5 mm when it is loaded with an initial load of 10 kg up to a final load of 130 kg. Such compression deformation may be controlled mainly by the amount of the metal salt of the unsaturated carboxylic acid, but it may also be controlled by the amounts of other chemicals, curing conditions etc. By whichever method it may be controlled, if the deformation of the core exceeds 3.5 mm, the rebound coefficient decreases and the flight performance is inferior. Basically, the ball is too soft and heavy and its shot feel is insecure and its durability is lower. On the contrary, if the deformation is less than 2.8 mm, the ball is too hard and the shot feel is inferior.

By covering the core obtained above with a cover having a thickness of from 1.5 to 2.1 mm, a two-piece golf ball is obtained. The cover is generally made from a cover composition which mainly comprises an ionomer resin and, as necessary, a filler or coloring agent (for example, titanium dioxide, barium sulfate, etc.). When the thickness of the cover is less than 1.5 mm, the ball spins easily and the shot feel is closer to that of a one-piece golf ball. When it is thicker than 2.1 mm, the shot feel is inferior.

In the present invention, it is preferred to adjust the stiffness of the cover to within the range of 3,000 to 4,500 kg/cm^2. When it is less than 3,000 kg/cm^2, the cover is too flexible and the ball spins easily and the shot feel is soft, heavy and insecure. Whereas if it exceeds 4,500 kg/cm^2, the cover is hard and gains a heavy shot feel.

The method to coat the ionomer resin cover on the core is well known and it is generally executed by injection molding.

EXAMPLES

The present invention is described in further detail according to Examples. However, the present invention is not limited to these Examples.

Examples 1 - 3 and Comparative Examples 1 - 4

A rubber composition was obtained by kneadding the rubber composition for the core shown in Table 1. Thus obtained rubber composition was cured and molded under the conditions given in Table 1. Hardness distribution and compression strength of thus obtained core are shown in Table 1.

The cover obtained by the ordinary method with the composition shown in Table 2 was covered with the aforesaid core. Stiffness and thickness of the cover used are shown in Table 2.

Table 3 shows the hardness (indicated by PAG) durability index, rebound coefficient, flight characteristics, such as launch angle, spin, carry etc. and results of hit feeling evaluation.

Table 1

Core								
		Ex. 1	Ex. 2	Ex.3	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex. 4
Formulation	BR-01*1	100	100	100	100	100	100	100
	Zinc diacrylate	31	29	27	31	25	31	31
	Zinc oxide	17.5	18.2	19.0	20.0	20.0	20.4	16.6
	Antioxidant	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	Dicumyl peroxide	2.2	2.2	2.2	2.2	2.0	1.8	2.3
Condition of curing	Temperature	155 °C	155 °C	155 °C	145 °C	160 °C	160 °C	152 °C
	Period of time	25 min.	25 min.	25 min.	40 min.	25 min.	25 min.	25min.
Hardness distribution	Center	71	65	60	70	56	62	65
	5mm from center	76	73	70	76	67	75	76
	10mm from center	76	73	70	81	67	75	76
	15mm from cener	86	84	79	83	75	79	86
	Surface	87	85	80	78	77	85	86
Compression	(mm)	2.9	3.1	3.4	2.6	3.7	3.2	2.7

*1 Butadiene rubber available from Japan Synthetic Rubber Co., Ltd.

Table 2

Cover								
Formulation*2	HIMILAN 1076	50	50	50	50	50	50	50
	HIMILAN 1605	50	50	50	50	50	50	50
Stiffness*3	23 °C X 2 weeks	3300	3300	3300	3300	3300	3300	3300
Thickness	(mm)	1.9	1.9	1.9	1.9	1.9	2.3	1.4

*2 2 wt parts of titanium oxide (TiO_2) was added to 100 wt parts of ionomer resin and coloring was conducted by an extruder to prepare a resin composition used for the cover.

*3 Stiffness was measured by a Stiffness Tester manufactured by Toyo Seiki Co., Ltd. A specimen was a flat plate made by press-molding and measurement was made after leaving the specimen for 2 weeks at 23 °C and 50 % humidity.

Table 3

Ball evaluation							
	Ex.1	Ex.2	Ex.3	Comp. Ex.1	Comp. Ex.2	Comp. Ex.3	Comp. Ex.4
Hardness (PGA)	105	100	95	110	88	100	92
Durability index*4	100	99	97	115	75	105	80
Rebound coefficient (45 m/s)	0.7820	0.7810	0.7800	0.7830	0.7720	0.7790	0.7735
Flying characteristics*5							
Launch angle (°)	12	12.2	12.5	11.4	12.8	12	10
Spin (rpm)	2600	2580	2550	2800	2500	2600	3200
Carry (yard)	230	230	230	230.5	227	228	220
Feeling evaluation	Light, soft and good	Light, soft and good	Light, soft and good	Hard	Too soft and heavy	Slightly hard and feel hardness cover	Soft, heavy and of dull

*4. Durability index: Withstand frequency of impact given to the specimen in Example 1 is deemed 100. Frequency of impact is the frequency of impact given until breaking of ball occurs, by shooting out the ball at the speed of 45 m/sec. by a swing robot manufactured by True Temper Co.

*5. 45 m/sec. W1 flight (flight charactetristics): The value obtained in the test to shoot out a ball by W1 (No. 1 Wood) at 45 m/sec. using the swing robot.

As it is evident from the results of Tables 1, 2 and 3, the balls of Examples 1 - 3 are light, soft, gives good hit feeling and their characteristics are closer to those of thread - wound golf balls. Durability and flight performance are also good.

The golf ball of Comparative Example 1 has the core with small compression strength (2.6 m/m), hardness of the ball is high, and the hit feeling is hard and inferior.

The ball of Comparative Example 2 has a large core compression strength (3.7 mm) and low hardness, and it is too soft and heavy and its hit feeling is insecure and inferior. Durability is low.

The ball of Comparative Example 3 has thick cover and its hit feeling was hard and inferior.

The ball of Comparative Example 4 has thin cover, its hit feeling is closer to that of one piece golf ball and its hit feeling is soft and heavy. The ball is easy to catch spin and has poor flight performance and durability.

The two-piece golf ball of the present invention has hit feeling close to that of thread-wound golf ball and its flight performance is the one specific to the two-piece golf ball and it has preferred characteristics as a golf ball in regard to both flight performance and hit feeling.

Claims

1. A two-piece golf ball comprising a core formed from a rubber composition comprising a base rubber, a co-crosslinking agent and an organic peroxide, and a cover covering the core, wherein the core has the following hardness distribution when measured by a JIS-C hardness meter:

(1) hardness at the center	58 to 73
(2) hardness at 5 to 10 mm from the center	68 to 78
(3) hardness at 15 mm from the center	76 to 88
(4) surface hardness	78 to 88

wherein in the hardness distribution, hardness (2) is substantially constant being within the above range, of which the tolerance is within ± 3 and the other values satisfy the relation of (1) < (2) < (3) ≤ (4), and wherein the compression deformation of the core is in the range of from 2.8 to 3.5 mm when pressurized by an initial load of 10 kg up to a final load of 130 kg and the cover has a thickness of 1.5 to 2.1 mm.

2. A golf ball as claimed in claim 1 wherein the core is made from a rubber composition which comprises cis-1,4-butadiene rubber, zinc diacrylate and dicumyl peroxide.

3. A golf ball as claimed in claim 2 wherein the rubber composition further comprises a filler and an antioxidant.

4. A golf ball as claimed in any one of the preceding claims wherein the cover is formed from an ionomer resin and a filler.

5. A golf ball as claimed in any one of the preceding claims wherein the cover has a stiffness in the range of from 3,000 to 4,500 kg/cm^2.

Patentansprüche

1. Zweiteiliger Golfball, umfassend einen Kern, der aus einer Kautschukzusammensetzung erzeugt wurde, die einen Grundkautschuk, ein Co-Vernetzungsmittel und ein organisches Peroxid umfaßt, sowie eine Ummantelung zum Umhüllen des Kerns, wobei der Kern die folgende Härteverteilung aufweist, wenn diese mit einem JIS-C Härtemessgerät gemessen wird:

(1) Härte im Zentrum	58 bis 73
(2) Härte in 5 bis 10 mm Abstand vom Zentrum	68 bis 78
(3) Härte in 15 mm Abstand vom Zentrum	76 bis 88
(4) Härte an der Oberfläche	78 bis 88

wobei in der Härteverteilung die Härte (2) innerhalb des vorstehenden Bereichs, dessen Toleranz ±3 beträgt, im wesentlichen konstant ist, und die anderen Werte die Beziehung (1) < (2) < (3) ≤ (4) erfüllen, und wobei die Druckverformung des Kerns, wenn ein Druck mit einer Anfangslast von 10 kg bis zu einer Endlast von 130 kg ausgeübt wird, im Bereich von 2,8 bis 3,5 mm liegt, und die Ummantelung eine Dicke von 1,5 bis 2,1 mm besitzt.

2. Golfball nach Anspruch 1, wobei der Kern aus einer Kautschukzusammensetzung besteht, umfassend cis-1,4-Butadienkautschuk, Zinkdiacrylat und Dicumylperoxid.

3. Golfball nach Anspruch 2, wobei die Kautschukzusammensetzung ferner einen Füllstoff und ein Antioxidans umfaßt.

4. Golfball nach einem der vorstehenden Ansprüche, wobei die Ummantelung aus einem Ionomerharz und einem Füllstoff erzeugt wird.

5. Golfball nach einem der vorstehenden Ansprüche, wobei die Ummantelung eine Steifheit im Bereich von 3.000 bis 4.500 kg/cm^2 besitzt.

Revendications

1. Balle de golf en deux morceaux comprenant un coeur formé à partir d'une composition de caoutchouc comprenant un caoutchouc de base, un agent de co-réticulation et un peroxyde organique, et une enveloppe recouvrant le coeur, dans laquelle le coeur a la distribution de dureté suivante lorsqu'elle est mesurée par un dispositif de mesure de dureté conforme à la norme JIS-C :

(1) dureté au centre :	58 à 73
(2) dureté à 5-10 mm du centre :	68 à 78
(3) dureté à 15 mm du centre :	76 à 88
(4) dureté en surface :	78 à 88

dans laquelle, dans la distribution de dureté, la dureté (2) est pratiquement constante à l'intérieur de l'inter-

valle ci-dessus, dont la tolérance est de ± 3, et les autres valeurs satisfont à la relation suivante : (1) < (2) < (3) ≤ (4), et dans laquelle la déformation par compression du coeur est située dans l'intervalle allant de 2,8 à 3,5 mm lors d'une pression par une charge initiale de 10 kg jusqu'à une charge finale de 130 kg et l'enveloppe a une épaisseur de 1,5 à 2,1 mm.

2. Balle de golf selon la revendication 1, dans laquelle le coeur est fait à partir d'une composition de caoutchouc qui comprend du caoutchouc de cis-1,4-butadiène, du diacrylate de zinc et du peroxyde de dicumyle.

3. Balle de golf selon la revendication 2, dans laquelle la composition de caoutchouc comprend en outre une charge et un antioxydant.

4. Balle de golf selon l'une quelconque des revendications précédentes, dans laquelle l'enveloppe est formée à partir d'une résine ionomère et d'une charge.

5. Balle de golf selon l'une quelconque des revendications précédentes, dans laquelle l'enveloppe a une rigidité située dans l'intervalle allant de 3000 à 4500 kg/cm^2.

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(54) Golf ball with cover formed from hard and soft ionomer resins.

(57) A golf ball is provided with a cover which is formed from a blend of lithium ionomer resin having a flexural modulus of at least 60,000 psi and a zinc ionomer resin having a flexural modulus within the range of 2800 to 8500 psi.

EP 0 630 665 A2

Background

This invention relates to golf balls, and, more particularly, to a golf ball having a cover which is formed from a blend of hard and soft ionomer resins. More particularly, the cover is formed from a blend of hard lithium ionomer resin and soft zinc ionomer resin.

Golf balls which are currently available fall into two general categories -- balls which include a balata cover and balls which include a more durable, cut-resistant cover. Balata covers are made from natural balata, synthetic balata, or a blend of natural and synthetic balata. Natural rubber or other elastomers may also be included. Synthetic balata is trans polyisoprene and is commonly sold under the designation TP-301 available from Kuraray Isoprene Company Ltd.

Most cut-resistant covers utilize Surlyn ionomers, which are ionic copolymers available from E.I. du Pont de Nemours & Co. Surlyn ionomers are copolymers of olefin, typically ethylene, and an alpha-beta ethylenically unsaturated carboxylic acid, such as methacrylic acid. Neutralization of a number of the acid groups is effected with metal ions, such as sodium, zinc, lithium, and magnesium. DuPont's U.S. Patent No. 3,264,272 describes procedures for manufacturing ionic copolymers. Ionic copolymers manufactured in accordance with U.S. Patent No. 3,264,272 may have a flexural modulus of from about 14,000 to about 100,000 psi as measured in accordance with ASTM method D-790. DuPont's U.S. Patent No. 4,690,981 describes ionic copolymers which include a softening comonomer. Ionic copolymers produced in accordance with U.S. Patent No. 4,690,981 are considered "soft" ionic copolymers and have a flexural modulus of about 2800 to about 8500 psi. The disclosures of Patent Nos. 3,264,272 and 4,690,981 are incorporated herein by reference.

Other cut-resistant materials which can be used in golf ball covers are ionic copolymers or ionomers available from Exxon under the name Iotek, which are similar to Surlyn ionomers except that acrylic acid is used rather than methacrylic acid.

The ionomer resins generally fall into three categories which are characterized by hardness or stiffness -- standard, high modulus, and low modulus. The standard resins have a flexural modulus in the range of about 30,000 to about 55,000 psi as measured by ASTM Method D-790. (Standard resins are referred to as "hard Surlyns" in U.S. Patent No. 4,884,814.) The high modulus resins have a flexural modulus in the range of about 55,000 to about 100,000 psi. The low modulus resins have a flexural modulus in the range of about 2800 to about 8500 psi.

Standard Surlyn resins include 8940 (sodium), 9910 (zinc), 7930 (lithium). Standard Iotek resins include 8000 (sodium), 8020 (sodium), 8030 (sodium), 4000 (zinc), and 4010 (zinc).

Low modulus ionomers are described in U.S. Patent 4,690,981 and include a softening comonomer. Specific low modulus Surlyn resins include 8120 (sodium), 8320 (sodium), and 9320 (zinc).

Specific high modulus Surlyn resin include 8220 (sodium), 8240 (sodium), 9220 (zinc), 7930 (lithium), and 9740 (lithium).

The term "3 piece" is commonly used to refer to a golf ball which has a center, a layer of elastic windings over the center, and a cover. The term "2 piece" is used to refer to a golf ball which has a solid core and a cover. Conventional balata-covered balls are 3 piece balls. Ionomer-covered balls an be either 3 piece or 2 piece balls.

A number of golfers, primarily professional and low handicap golfers, prefer balata-covered balls because of the higher spin rate, control, "feel," and "click" which balata provides. "Feel" is the overall sensation imparted to a golfer when the ball is hit, and "click" refers to the sound made when the clubhead hits the ball. However, balata-covered balls are more expensive and are less resistant to cutting than ionomer-covered balls.

Originally, ionomer-covered balls felt harder and had a much lower spin rate than balata-covered balls. In order to produce softer balls with higher spin rates, ionomers with lower flexural moduli were used. Some balls used various blends of a hard ionomer having a relatively high flexural modulus and a soft ionomer having a relatively low flexural modulus. However, varying one of the physical properties of one of the ionomers used in a golf ball cover usually affects one or more of the performance parameters of a golf ball, including feel, spin rate, initial velocity, distance, cut resistance, durability, etc. If a soft ionomer is used to improve feel and spin, other factors such as distance and cut resistance are often adversely affected. Also, the relative amounts of the different ionomers in the blend can also affect the properties of the ball.

U.S. Patent No. 3,819,768 describes early ionomer covers for golf balls. The specific covers described in the patent are made from a blend of sodium Surlyn ionomer and zinc Surlyn ionomer. The patent also describes using other ions, including lithium ions, to neutralize the ionomer. It is believed that all of the ionomers which were commercially available at that time were relatively hard ionomers which had a flexural modulus of at least 50,000 psi.

U.S Patent No. 4,431,193 describes a golf ball with a two-layer cover. The inner layer is formed from a hard ionomer resin having a high flexural modulus, and the outer layer is formed from a soft ionomer resin having a low flexural modulus. The specific hard ionomer described in Surlyn 1605, which is a sodium Surlyn having a flexural modulus of about 51,000. The specific soft ionomer described is Surlyn 1855, which is a zinc Surlyn having a flexural modulus of about 14,000.

U.S. Patent No. 4,884,814 describes a golf ball cover which is formed from a blend of hard Surlyn and soft Surlyn. The hard Surlyn is described as a high modulus ionomer having a flexural modulus of from about 30,000 to 55,000 psi, and the soft Surlyn is a low modulus ionomer having a flexural modulus of from about 3,000 to about 7,000 psi. The specific ionomers described in the patent are sodium and zinc.

U.S. Patent No. 5,120,791 describes a golf ball cover which is formed from a blend of a hard sodium or zinc ionomer and a soft acrylic acid based sodium or zinc ionomer. The hard ionomer is described as having a flexural modulus of from about 15,000 to about 70,000 psi, and the soft ionomer is described as having a flexural modulus of from about 2,000 to 10,000 psi.

Since about 1986 DuPont has been offering lithium Surlyn to golf ball manufacturers. DuPont Research Disclosure No. 27221 describes golf ball covers using lithium ionomers or blends of lithium ionomers and other ionomers. An early DuPont lithium Surlyn which was used in golf ball covers was AD-8118 Surlyn, which has a flexural modulus of about 61,000 psi. Wilson Staff three piece golf balls sold by Wilson Sporting Goods Co. in 1988 had covers made from a blend of lithium Surlyn AD-8118 and low modulus sodium Surlyn 8265. The sodium Surlyn 8265 had a flexural modulus of about 7000 psi.

U.S. Patent No. 5,000,459 describes a golf ball cover which is formed from a blend of lithium and sodium Surlyn. The specific lithium Surlyn described in the patent is 8118. The sodium Surlyns described in the patent are 8660 and 8920. The sodium Surlyns 8660 and 8920 have flexural moduli of about 34,000 psi and 55,000 psi, respectively.

U.S. Patent No. 5,068,151 describes a golf ball cover formed from either lithium ionomer or a blend of lithium ionomer and di- or tri-valent metal neutralized ionomer, for example, zinc ionomer. The patent does not describe the flexural modulus of the ionomers, but it does describe the Shore D hardness and the melt index. The Shore D hardness of the lithium ionomer was 60 to 80, and the melt index as 0.5 to 5.0. The Shore D hardness and the melt index of the zinc ionomer was also 60 to 80 and 0.5 to 5.0.

The foregoing description of the prior art evidences intense activity by golf ball manufacturers to optimize golf ball covers to provide a golf ball with good cut resistance, feel, spin, and distance. However, because improvement in one property often results in a decrease in another property, golf ball companies have continued to search for ways to improve the performance of golf balls.

Summary of the Invention

I have found that excellent results can be obtained by utilizing a golf ball cover which is made from a blend of a high modulus or hard lithium ionomer and a low modulus or soft zinc ionomer. The preferred ionomers are lithium Surlyn 7930 and zinc Surlyn 9320, and the preferred blend is a 50/50 blend of the hard and soft ionomers. Lithium Surlyn 7930 has a flexural modulus of about 67,000 psi, and zinc Surlyn 9320 has a flexural modulus of about 3500 psi Golf balls utilizing such a cover have a soft feel and a high spin rate, comparable to a balata-covered ball, yet have good distance and cut resistance.

Description of the Drawing

Figure 1 is a cross section of a two piece ball formed in accordance with the invention; and
Figure 2 is a cross section of a three piece ball formed in accordance with the invention.

Description of Specific Embodiments of the Invention

Figure 1 illustrates a two piece golf ball 10 which includes a solid core 11 and a cover 12. The cover is formed primarily from a blend of a relatively hard ionomer having a high flexural modulus and a relatively soft ionomer having a low flexural modulus. The cover may also include other conventional ingredients such as zinc oxide, titanium dioxide, blue toner, and optical brightener. The thickness of the cover is conventional and within the range of about .085 to .090 inch. The diameter of the core is about 1.500 to 1.510 inch and the outside diameter of the ball is about 1.680 inch.

Figure 2 illustrates a three piece golf ball 15 which includes a wound core 16 which comprises a center 17 and a layer 18 of windings of elastic thread. The center may be solid or a liquid-filled balloon. Such wound cores are also conventional. A cover 19 is formed primarily from a blend of a relatively hard ionomer

and a relatively soft ionomer. The cover may also include other conventional ingredients. The thickness of the cover is within the range of about .065 to .075 inch. The outside diameter of the ball is about 1.680 inch. I have found that a blend of a high modulus, hard lithium ionomer having a flexural modulus of at least 60,000 psi and a low modulus, soft zinc ionomer having a flexural modulus within the range of about 2800 to 8500 psi provides a golf ball cover which not only has good cut resistance but also provides good feel, a high spin rate, and good distance. The ratio of the high modulus and low modulus ionomers can vary within a range of about 60/40 to 40/60. The preferred embodiment uses lithium Surlyn 7930 and zinc Surlyn 9320 in a ratio of about 50/50.

Lithium Surlyn 7930 and zinc Surlyn 9320 have the physical properties set forth in Table I.

TABLE I

	units	7930	9320
flexural modulus	kpsi	67	3.5
melt flow index	g/10 min	1.8	0.6
specific gravity		0.94	0.94
tensile strength	kpsi	3.8	2.5
elongation	%	290	600
hardness, Shore D (ASTM D-2240)		68	40

Example I

Two-piece golf balls were made using cores having the composition described in Table II.

TABLE II

Composition of Core (Parts by Weight)	
Polybutadiene	100.0
ZDA (zinc diacrylate)	33.0
ZnO	21.0
A02246	1.0
Dicumyl Peroxide	2.25
Total	157.25

A02246 is an antioxidant available from R.T. Vanderbilt Co. of Norwalk, Connecticut under the trade name Vanox MBPC.

The covers for the golf balls had the composition described in Table III.

TABLE III

Composition of Cover (Parts by Weight)	
Surlyn 7930	50.0
Surlyn 9320 (AD8270)	50.0
Color Concentrate #29835R7	8.0
Total	108.0

The color concentrate of Table III had the following composition (parts by weight):

Surlyn 8940	100.000
TiO_2	72.423
Ultramarine Blue	.006
Ultramarine Violet	.006

Ultramarine Blue and Ultramarine Violet are toners available from Whittaker, Clark & Daniels, Inc. of South Plainfield, New Jersey.

The cover composition was injection molded over the solid core in the conventional manner. Alternatively, and also conventionally, the cover material can be injection molded into hemispherical half shells, and two half shells can be compression molded over a solid or wound core.

The molded cover material had a flexural modulus of about 14,920 psi and a Shore D hardness of about 57.

The cover of the Example I balls is referred to as a 50/50 blend of Surlyn 7930 and Surlyn 9320. In fact, the Surlyn composition of the cover also includes the Surlyn contained in the color concentrate or master batch which contains additional Surlyn as well as the other ingredients of the cover.

Golf balls of Example I were compared with a commercial ball which is sold under the name Tour Edition 100. The Tour Edition 100 ball is advertised as a cut-resistant ball which has feel and playing characteristics similar to balata-covered balls. The comparative physical data is set forth in Table IV.

TABLE IV

	diameter (inches)	weight (grams)	compression	durability	initial velocity (feet/sec)
Tour Edition	1.679	45.5	115.8	100	248.7
Example I	1.678	45.4	93.8	96.8	248.5

Compression is a measure of a golf ball's deflection at a specified load. A universal piece of testing equipment used in the golf ball industry for measuring compression is a ATTI compression tester as purchased from Atti Engineering Corp., 108-110 36th St., Union City, New Jersey 07087.

Durability is a measure of a golf ball to withstand repeated impacts against a thick metal plate @ 175 FPS. Wilson's procedure is to subject 20 balls to repeated impacts up to 100, then average the # of hits to failure for each group.

Initial velocity is measured in accordance with the standards of the United States Golf Association.

The golf balls were flight tested with an automatic hitting machine using drivers having various lofts (launch angles), a 5 iron, and a 9 iron. The hitting machine was adjusted to swing the drivers at 150 feet per second (fps) at impact (hard driver) and at 130 fps (soft driver). The comparative flight test data is formed in Table V.

TABLE V

Hard Driver (150 fps) - 7° Launch Angle

	Carry	Difference	Total	Difference
Tour Edition 100	251.2	base	264.7	base
Example I	251.5	+0.3	261.8	-2.9

Hard Driver (150 fps) - 9° Launch Angle

	Carry	Difference	Total	Difference
Tour Edition 100	260.1	base	264.0	base
Example I	261.9	+1.8	271.0	+7.0

Hard Driver (150 fps) - 11° Launch Angle

	Carry	Difference	Total	Difference
Tour Edition 100	251.4	base	253.4	base
Example I	256.4	+5.0	260.3	+6.9

Soft Driver (130 fps) - 10° Launch Angle

	Carry	Difference	Total	Difference
Tour Edition 100	214.1	base	218.1	base
Example I	217.7	+3.6	226.0	+7.9

5 iron (110 fps) - 15° Launch Angle

	Carry	Difference	Total	Difference
Tour Edition 100	156.3	base	164.2	base
Example I	161.6	+5.3	171.8	+7.6

9 iron (80 fps) - 19° Launch Angle

	Carry	Difference	Total	Difference
Tour Edition 100	119.6	base	122.7	base
Example I	120.1	+1.5	123.7	+1.0

Spin Comparison

	Hard Driver	9 Iron
Tour Edition	3850 (RPM)	8930 (RPM)
Example I	3460 (RPM)	7880 (RPM)

Coefficient of Restitution (C.O.R.)

	150FPS	175FPS	200FPS
Tour Edition	.7442	.7156	.6847
Example I	.7749	.7445	.7141

Cut Resistance

Balls formed in accordance with Example I were subjected to the standard Wilson cut resistance test. The cut resistance test is conducted using a Tru Temper driving Machine. The test club used is a pitching wedge. Six (6) balls of each type are tested and hit one time each approximately 1/4 inch above the centerline of the ball, (random orientation), at standard clubhead velocities.

Factor	Description
10	No visible mark
9	Must search to find mark
8	Visible dent
7	Feel with fingernail
6	Fingernail inserts - cut
5	Fingernail inserts to core - core not visible
4	Core visible - core not cut
3	Core just cut
2	Core cut deep
1	Core destroyed

The factors of the six (6) golf balls of each type are averaged to obtain an overall factor. The golf balls are evaluated by relative comparison with other golf balls of known cut resistance.

The inventive balls formed in accordance with Example I were compared to Tour Edition, the comparative cut resistance data is as follows:

Ball I.D.	Cut resistance factor
Tour Edition	6.6
Example I	8.2

The data presented illustrates that the inventive ball (Example I), is significantly improved for cut resistance over the Tour Edition 100 ball.

The flight test data comparison of the Tour Edition 100 ball and the balls of Example I shows that the hard driver hit at the average launch angle of 9 degrees, soft driver and 5 iron hits are significantly longer in both carry and total flight distances than the Tour Edition 100 ball. The Example I ball has a higher C.O.R. than Tour Edition 100.

While in the foregoing specification a detailed description of specific embodiments of the invention were set forth for the purpose of illustration, it will be understood that many of the details herein given may be

varied considerably by those skilled in the art without departing from the spirit and scope of the invention.

Claims

1. A golf ball comprising a core and a cover, the cover comprising a blend of a lithium ionomer resin having a flexural modulus of at least 60,000 psi and a zinc ionomer resin having a flexural modulus within the range of about 2800 to 8500 psi.

2. The golf ball of claim 1 in which the cover includes from 60 to 40 parts by weight of the lithium ionomer resin and from 40 to 60 parts parts by weight of the zinc ionomer resin.

3. The golf ball of claim 1 in which the cover includes from about 50 parts by weight of the lithium ionomer resin and from about 50 parts parts by weight of the zinc ionomer resin.

4. The golf ball of claim 1 in which the flexural modulus of the zinc ionomer resin is about 3500 psi.

5. The golf ball of claim 4 in which the flexural modulus of the lithium ionomer resin is about 67,000 psi.

6. The golf ball of claim 1 in which the lithium ionomer resin is lithium Surlyn 7390 and the zinc ionomer resin is zinc Surlyn 9320.

7. The golf ball of claim 6 in which the cover includes from 60 to 40 parts by weight of the lithium ionomer resin and from 40 to 60 parts parts by weight of the zinc ionomer resin.

8. The golf ball of claim 6 in which the cover includes from about 50 parts by weight of the lithium ionomer resin and from about 50 parts parts by weight of the zinc ionomer resin.

FIG. 1

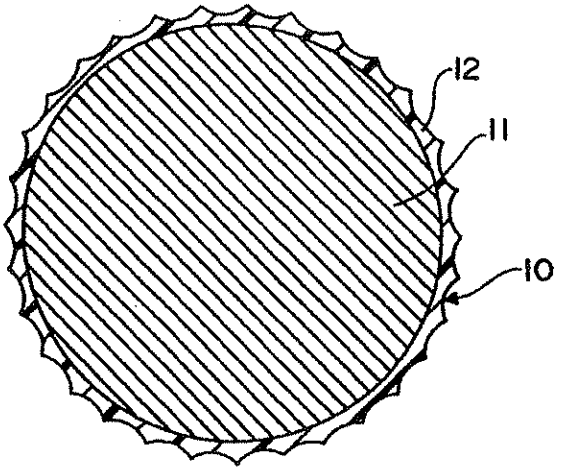
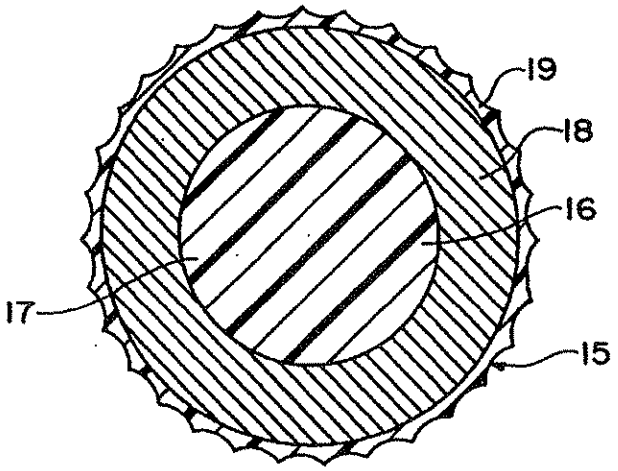


FIG. 2



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(54) **Golf ball with cover formed from hard and soft ionomer resins.**

(57) A golf ball is provided with a cover which is formed from a blend of lithium ionomer resin having a flexural modulus of at least 60,000 psi and a zinc ionomer resin having a flexural modulus within the range of 2800 to 8500 psi.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	GB-A-2 247 682 (SPALDING & EVENFLO COMPANIES INC) * page 7, line 12 - page 8, line 13; claims 1,8 *	1-8	A63B37/00
Y,D	US-A-5 068 151 (NAKAMURA) * examples 3,4 *	1-8	
Y	EP-A-0 490 619 (ACUSHNET COMPANY) * page 1, line 30-41 * * page 2, line 5-20; claims *	1-8	
A	EP-A-0 470 854 (SUMITOMO RUBBER INDUSTRIES LIMITED) * claims; example 3 *	1-8	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 September 1995	Giménez Burgos, R

EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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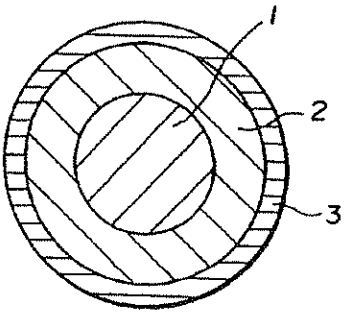
(54) Golf balls.

(57) In a three-piece solid golf ball comprising a center core, an intermediate layer, and a cover, the center core (1) has a diameter of at least 29 mm and a specific gravity of less than 1.4, the intermediate layer (2) has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale, and the cover (3) has a thickness of 1-3 mm. The ball has a good total balance of properties in that feeling and controllability are improved at no sacrifice of flying performance and durability.

FIG.1



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This specification relates to golf balls.

Prior Art

Among a variety of golf balls, thread-wound golf balls and solid golf balls are now popular. The solid golf balls are currently increasing to be a mainstream. Among them, two-piece solid golf balls consisting of a core and a cover are most widespread.

Most amateur golfers are fond of two-piece solid golf balls which have excellent flying performance and durability although these balls have the disadvantages of a very hard feel on hitting and low control due to rapid ball separation on hitting. For this reason, many of professional golfers and skilled amateur golfers who impose weight on feeling and control prefer wound golf balls, especially wound golf balls using a soft balata cover, to two-piece solid golf balls. The wound golf balls are superior in feeling and control, but inferior in flying distance and durability to the two-piece solid golf balls.

Under the present situation that two-piece solid golf balls and wound golf balls have contradictory characteristics as mentioned above, players make a choice of golf balls depending on their own skill and taste.

In order to develop solid golf balls having a hitting feel approximate to the wound golf balls, two-piece solid golf balls of soft type have been considered. For such two-piece solid golf balls of soft type, soft cores must be used. If the cores are soft, however, repulsion becomes low with a concomitant loss of flying performance and durability is considerably deteriorated. That is, the superior flying performance and durability which are characteristic of two-piece solid golf balls are lost, and in an extreme case, the balls become unacceptable for practical use.

Controllability, which is required even on full shots with drivers, is most important on control shots like approach shots. In an exemplary situation that the next shot should fly beyond the bunker and a short distance from the green edge to the cup, the player who is either professional or amateur will naturally wish to hit a ball with a minimal run. Such controllability of a golf ball largely depends on spin properties.

On a full shot with a club having a relatively large loft, the club loft is more dominant than the ball itself so that almost all balls are given an appropriate amount of spin and few balls overrun. However, on a approach shot over a short distance of 30 or 50 yards, balls will significantly vary in run or controllability. The major factor causing such a difference is not a basic structure, but the identity of cover material. In two-piece solid golf balls, however, covers made of soft material are effective for improving controllability but detrimental for gaining flying distance.

An aim herein is to provide a novel and useful solid golf ball construction. A preferred aim is to achieve a good feel and controllability while maintaining the good flying performance and durability which are characteristic of solid golf balls.

In connection with a solid golf ball having a core forming the center and a cover forming the outermost layer, we have found that by providing a relatively hard intermediate layer between the center core and the cover,

the center core can be made relatively soft so as to improve feeling and controllability without deteriorating flying performance and durability. The feeling and controllability can be improved in a favorable way.

Preferably the dimensions and densities of these elements are adjusted as follows. An intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale is formed around a center core having a diameter of at least 29 mm and a specific gravity of less than 1.4 and greater than the intermediate layer specific gravity and a cover having a thickness of 1 to 3 mm is formed on the outer surface of the intermediate layer to complete a solid golf ball. Then even when the center core is softened to a JIS C scale hardness of 45 to 80 and the cover softened to a JIS C scale hardness of 50 to 85, good feeling and controllability can be achieved with little or no loss of flying distance and durability. Further when the intermediate layer is formed of a resin composition based on a high repulsion ionomer resin, the hitting feel and controllability can be further improved with little or no loss of flying distance and durability.

A specific proposal herein is therefore a three-piece solid golf ball comprising a center core, an intermediate layer, and a cover wherein the center core has a diameter of at least 29 mm and a specific gravity of less than 1.4, the intermediate layer has a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale, and the cover has a thickness of 1 to 3 mm. The specific gravity of the intermediate layer is lower than the specific gravity of the center core. In one preferred embodiment, the intermediate layer is formed of a composition based on a high repulsion ionomer resin.

BRIEF DESCRIPTION OF THE DRAWING

The only figure, FIG. 1 is a schematic cross section of a three-piece solid golf ball.

EXPLANATIONS; PREFERRED AND OPTIONAL FEATURES

Referring to FIG. 1, there is schematically illustrated a typical three-piece solid golf ball embodying our new concepts. The ball includes a spherical center core 1 forming the center of the ball and a cover 3 forming the outermost layer of the ball. A relatively hard intermediate layer 2 is disposed between the core 1 and the cover 3. The size and specific gravity of the core 1, intermediate layer 2, and cover 3 are preferably in the specific ranges explained below (which may be selected individually, independently of one another).

The center core generally has a diameter of at least 29 mm, preferably 29 to 37 mm and a specific gravity of less than 1.4, preferably 1.05 to 1.38. With a diameter of less than 29 mm, the intermediate layer must be relatively thick with losses of repulsion and feeling. With a specific gravity of 1.4 or more, the ball has a heavier weight which may exceed the weight requirement for golf balls.

On an impact entailing substantial deformation as found on driver shots, the player gets a feeling which largely depends on the hardness of the center core 1 and varies with the club head speed given by the player. Therefore, the hardness of the center core 1 should be set in accordance with the head speed of the target players. In this sense, the center core hardness is not particularly limited although it preferably ranges from 45 to 80, more preferably from 60 to 80 on JIS C scale (at the center core surface).

The center core 1 may be formed from a well-known rubber composition comprising a base rubber, co-crosslinking agent and peroxide through heating, pressing and molding steps. The base rubber may be one conventionally used in solid golf balls and preferably is selected from polybutadiene rubber and mixtures of polybutadiene rubber and polyisoprene rubber. Use of 1,4-polybutadiene rubber containing more than 90% of cis structure is preferred for high repulsion. The co-crosslinking agents used in conventional solid golf balls include zinc and magnesium salts of unsaturated fatty acids such as methacrylic acid and acrylic acid and esters of unsaturated fatty acids such as trimethyl-propane trimethacrylate and they may be used.

Zinc acrylate is preferred for high repulsion. The co-crosslinking agent is blended in amounts of about 15 to 30 parts by weight per 100 parts by weight of the base rubber. The peroxide may be selected from a variety of peroxides, preferably dicumyl peroxide and mixtures of dicumyl peroxide and 1,1-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane. The peroxide is blended in amounts of about 0.5 to 1 part by weight per 100 parts by weight of the base rubber. If desired, zinc oxide and barium sulfate may be blended in the rubber composition for specific gravity adjustment while antioxidants may also be blended.

The intermediate layer 2 generally has a radial thickness of at least 1 mm, preferably 1.5 to 3.5 mm, a specific gravity of less than 1.2, preferably 0.9 to 1 and lower than the center core specific gravity, and a hardness of at least 85, preferably 85 to 100 on JIS C scale. With a thickness of less than 1 mm, repulsion is lowered to reduce flying distance. With a specific gravity of 1.2 or more, the center core must have a relatively low specific gravity so that the golf ball may be increased in inertia moment and reduced in spin property and thus lose some controllability. Similar detrimental effect is observed when the intermediate layer specific gravity is greater than the center core specific gravity. A layer with a JIS C scale hardness of less than 85 detracts from flying performance. The intermediate layer preferably has an outer diameter of 38 to 41 mm though not limited thereto. Also preferably the difference in specific gravity between the center core and the intermediate layer is 0.1 or more, especially 0.1 to 0.5 though not limited thereto.

The intermediate layer 2 can be effective in compensating for lower repulsion of the center core 1 which is made soft. It may be formed of a relatively hard (JIS C scale hardness ≧ 85), repulsive material. Although the material is not critical, ionomer resins are preferred e.g. having the compositions of Himilan® 1706 or 1605 (commercially available from Mitsui-duPont Polychemical K.K.) or of Surlyn® (commercially available from E.I. du Pont). A 1:1 blend of Himilan 1706 and Himilan 1605 is most preferred. In addition to the ionomer resin, the composition of which the intermediate layer is formed may further contain weight control agents, for example, inorganic fillers such as zinc oxide and barium sulfate, coloring agents such as titanium dioxide, and other additives. The cover 3 generally has a radial thickness of 1 to 3 mm, preferably 1.5 to 2.5 mm. A cover of more than 3 mm thick is low in repulsion whereas a cover of less than 1 mm thick is low in durability such as cut resistance. Although the hardness of the cover 3 is not particularly limited, it is preferably set in a relatively soft range of 50 to 85, more preferably 60 to 85 on JIS C scale because in this range, good properties in all of repulsion (flying performance), durability and controllability are expected.

The cover 3 may be formed of resinous materials which are conventionally used as the cover of solid golf balls, preferably those materials which are relatively soft (JIS C scale hardness 50 to 85) and highly repulsive. Examples include ionomer resins such as Himilan® 1650 commercially available from Mitsui-duPont Polychemical K.K., Surlyn® 8120 commercially available from E.I. duPont, and mixtures thereof, thermoplastic polyester elastomers such as Hytrel® 4047 commercially available from Toray-duPont K.K., and balata resins. If necessary, inorganic fillers may be blended in these resins for coloring purposes.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation.

Examples and Comparative Examples

Using a center core, intermediate layer, and cover having the composition shown in Table 1, three-piece solid golf balls (Examples 1-6, Comparative Examples 1-3) were prepared. The center core was prepared by kneading the respective components in a roll mill and pressure molding at 155°C for 15 minutes. The intermediate layer was formed by injection molding so as to enclose the outer surface of the center core. The cover was formed around the intermediate layer by injection molding. The three-piece solid golf balls were completed in this way. The parameters associated with the core, intermediate layer and cover are shown in Table 2.

The golf balls were evaluated for spin characteristic, flying performance, feeling, and durability by the following tests. The results are shown in Table 2.

Spin characteristic

Using a swing robot manufactured by True Temper Co., the ball was hit by the driver at a head speed of 45 m/s (abbreviated as W1 HS45 in Table 2) and by the sand wedge at a head speed of 17.6 m/s (abbreviated as SW HS17.6 in Table 2). The ball spin (rpm) was observed using a science eye (manufactured by Bridgestone Corporation).

Feeling

Professional golfers evaluated a feeling on impact according to the following criterion.

- ○: good
- Δ: average
- ×: poor

Flying performance

In the spin and feeling tests, the flying distance the ball traveled was also measured. Total evaluation was made according to the following criterion.

- ○: good
- Δ: average
- ×: poor

Durability

Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/s until the ball was broken. With the number of hits counted, the ball was rated according to the following criterion.

- ○: good
- Δ: average
- ×: poor

Table 1

	Example						Comparative Example		
	1	2	3	4	5	6	1	2	3
Center core									
Cis-1,4-polybutadiene	100	100	100	100	100	100	100	100	100
Zinc acrylate	20	20	20	30	20	20	20	25	20
Zinc oxide	56	36	36	20	23	10	90	25	55
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Dicumyl peroxide	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Intermediate layer									
Himilan 1706	50	50	50	50	50	50	50	50	50
Himilan 1605	50	50	50	50	50	50	50	50	50
Cover									
Himilan 1650	50	50	50			50	50		50
Surlyn 8120	50	50	50			50	50		50
Hytrel 4047				100				100	
Trans-isoprene rubber					90				
Natural rubber					10				

Note:

The amounts of components blended are parts by weight and their proportion is independent among the center core, intermediate layer, and cover.

Table 2

	Example						Comparative Example		
	1	2	3	4	5	6	1	2	3
Center core									
Outer diameter, mm	31.52	35.28	35.28	35.28	35.29	36.40	27.68	35.24	31.52
Hardness, JIS C	66	66	66	79	66	66	66	73	66
Specific gravity	1.36	1.24	1.24	1.19	1.16	1.07	1.56	1.19	1.35
Intermediate layer									
Thickness, mm	3.4	1.7	2.2	2.2	1.7	2.0	5.7	1.8	1.6
Hardness, JIS C	91	91	91	91	91	91	91	82	91
Specific gravity	0.95	0.95	0.95	0.95	0.95	0.95	0.95	0.97	0.95
Outer diameter, mm	38.35	38.73	39.65	39.66	38.73	40.40	39.00	38.91	34.56
Cover									
Thickness, mm	2.2	2.0	1.5	1.5	2.0	1.8	1.8	1.9	4.0
Specific gravity	0.97	0.97	0.97	1.10	1.13	0.97	0.97	1.10	0.97
Hardness, JIS C	82	82	82	61	78	82	82	61	82
Ball									
Outer diameter, mm	42.68	42.67	42.67	42.70	42.70	44.00	42.65	42.63	42.65
Weight, g	45.50	45.45	45.50	45.55	45.53	45.60	45.50	45.55	45.50
Performance									
Spin (rpm) W1 HS45	3300	3020	3030	3920	3600	3030	3500	3600	3250
SW HS17.6	3900	4000	4300	6390	5800	4100	4100	4050	3500
Feeling	△	○	○	△	○	○	×	○	○
Flying performance	○	○	○	○	△	○	×	×	×
Durability	○	○	○	○	○	○	○	○	○

As is evident from Table 2, the three-piece solid golf balls, and particularly those with the preferred selected dimensions and densities etc. of their components, had a good balance of properties in that the center core and cover can be made soft so as to ensure a pleasant feeling and controllability (spin) without deteriorating flying performance and durability.

There has been described a three-piece solid golf ball which includes a core, intermediate layer and cover having controlled size, hardness and specific gravity so that the ball has a good total balance of properties in that a relatively soft center core and cover are used to ensure a pleasant feeling and controllability at no sacrifice of flying performance and durability.

Japanese Patent Application No. 5-193065 is incorporated herein by reference.

Although some preferred embodiment have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Claims

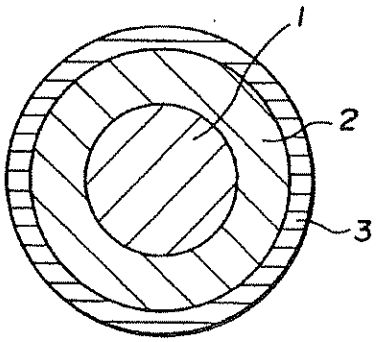
1. A three-piece solid golf ball comprising a center core, an intermediate layer, and a cover enclosing the core through the intermediate layer,
   said center core having a diameter of at least 29 mm and a specific gravity of less than 1.4,
   said intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of at least 85 on JIS C scale, the specific gravity of said intermediate layer being lower than the specific gravity of said center core, and
   said cover having a thickness of 1 to 3 mm.

2. The golf ball of claim 1 wherein said intermediate layer is formed of a high repulsion ionomer resin base composition.

3. The golf ball of claim 1 wherein said center core has a hardness of 45 to 80 on JIS C scale and said cover has a hardness of 50 to 85 on JIS C scale.

4. The golf ball of claim 1 wherein said center core is comprised of a polybutadiene base rubber composition.

FIG.1



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 5042

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	GB-A-2 228 874 (SUMITOMO RUBBER INDUSTRIES LTD) * page 2, line 23 - page 5, line 31; claims *	1-4	A63B37/00
A	GB-A-2 232 162 (SUMITOMO RUBBER INDUSTRIES LTD) * abstract; figures *	1	
A	GB-A-2 185 890 (KAMATARI CO. LTD) * abstract; claims *	1	
A	FR-A-2 666 018 (SALOMON (S.A.)) * abstract *	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

A63B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 October 1994	Giménez Burgos, R

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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(54) **Golf ball**

Golfbälle

Balles de golf

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Description

Prior Art

[0001] Golf balls of various structures are currently on the market. Among others, two-piece solid golf balls and thread-wound golf balls share the majority of the market. The two-piece solid golf ball has a rubber based core and an enclosing cover typically of ionomer resin while the thread-would golf ball is produced by winding thread rubber around a solid or liquid center and enclosing the center in a cover.

[0002] Most amateur golfers are fond of two-piece solid golf balls which have excellent flying performance and durability although these balls have the disadvantages of a very hard feel on hitting and low control due to rapid ball separation on hitting. For this reason, many of professional golfers and skilled amateur golfers prefer wound golf balls to two-piece solid golf balls. The wound golf balls are superior in feeling and control, but inferior in flying distance and durability to the two-piece solid golf balls.

[0003] Under the present situation that two-piece solid golf balls and wound golf balls have contradictory characteristics as mentioned above, players make a choice of golf balls depending on their own skill and taste.

[0004] In order to develop solid golf balls having a hitting feel approximate to the wound golf balls, two-piece solid golf balls of soft type have been considered. For such two-piece solid golf balls of soft type, soft cores must be used. If the cores are soft, however, repulsion becomes low with a concomitant loss of flying performance and durability is considerably deteriorated. That is, the superior flying performance and durability which are characteristic of two-piece solid golf balls are lost, and in an extreme case, the balls become unacceptable for practical use. Differently stated, since conventional two-piece solid golf balls have the structure which is determined by optimizing three parameters, softness, repulsion and durability, one of these parameters can be improved only at the sacrifice of the other parameters.

[0005] An aim herein is to provide a novel and useful solid golf ball construction. A preferred aim is to achieve a good feel while maintaining the good flying performance and durability which are characteristic of solid golf balls.

[0006] In connection with a solid golf ball having a core forming the center and a cover forming the outermost layer, we have found that by providing a soft intermediate layer between the center core and the cover, the center core can be made relatively soft so as to improve feeling without deteriorating flying performance and durability. The hitting feel can be improved in a favourable way.

[0007] We note that US-A-5253871/FR-A-2666018 describes examples of three-piece golf balls having an intermediate layer of amide block polyether. The cover layers on the exemplified balls have hardnesses of 43 to 47 Shore D; the prescribed general range is Shore D 40 to 55 : about 64 to about 80 on the JIS C scale.

[0008] In the present invention the dimensions and densities of these elements are adjusted as follows. An intermediate layer having a thickness of at least 1 mm, a specific gravity of less than 1.2, and a hardness of less than 80 on JIS C scale is formed around a center core having a diameter of at least 26 mm and a specific gravity of less than 1.4 and a cover having a thickness of 1 to 3 mm and a hardness of at least 85 on the JIS C scale is formed on the outer surface of the intermediate layer to complete a solid golf ball. Then even when the center core is softened to a JIS C scale hardness of 80 or less, an excellent feel can be achieved with little or no loss of flying distance and durability. Further, as the intermediate layer is formed of a resin composition based on a thermoplastic polyester elastomer, the hitting feel can be further improved with little or no loss of flying distance and durability.

BRIEF DESCRIPTION OF THE DRAWING

[0009] The only figure, FIG. 1 is a schematic cross section of a three-piece solid golf ball.

EXPLANATIONS; PREFERRED AND OPTIONAL FEATURES

[0010] Referring to FIG. 1, there is schematically illustrated a typical three-piece solid golf ball embodying our new concepts. The ball includes a spherical center core 1 forming the center of the ball and a cover 3 forming the outermost layer of the ball. A soft intermediate layer 2 is disposed between the core 1 and the cover 3. The size and specific gravity of the core 1, intermediate layer 2, and cover 3 are in the specific ranges explained below (which may be selected individually, independently of one another).

[0011] The center core generally has a diameter of at least 26 mm, preferably 27 to 37 mm and a specific gravity of less than 1.4, preferably 1 to 1.35. With a diameter of less than 26 mm, feeling is not fully improved by making the center core 1 to be soft and the ball starts to have less elastic repulsion so that the flying distance is reduced. With a specific gravity of 1.4 or more, the ball has a heavier weight which may exceed the weight requirement for golf balls.

[0012] On an impact entailing substantial deformation as found on driver shots, the player gets a feeling which largely depends on the hardness of the center core 1 and varies with the club head speed given by the player. Therefore, the hardness of the center core 1 should be set in accordance with the head speed of the target players. In this

sense, the center core hardness is not particularly limited although it preferably ranges up to 80, more preferably from 40 to 75 on JIS C scale (at the center core surface).

[0013] The center core 1 may be formed from a well-known rubber composition comprising a base rubber, co-crosslinking agent and peroxide through heating, pressing and molding steps. The base rubber may be one conventionally used in solid golf balls and preferably is selected from polybutadiene rubber and mixtures of polybutadiene rubber and polyisoprene rubber. Use of 1,4-polybutadiene rubber containing more than 90% of cis structure is preferred for high repulsion. The co-crosslinking agents used in conventional solid golf balls include zinc and magnesium salts of unsaturated fatty acids such as methacrylic acid and acrylic acid and esters of unsaturated fatty acids such as trimethylpropane trimethacrylate and they may be used. Zinc acrylate is preferred for high repulsion. The co-crosslinking agent is blended in amounts of about 10 to 27 parts by weight per 100 parts by weight of the base rubber. The peroxide may be selected from a variety of peroxides, preferably dicumyl peroxide and mixtures of dicumyl peroxide and 1,1,-bis(t-butylperoxy)-3,3,5-trimethylcyclohexane. The peroxide is blended in amounts of about 0.5 to 1 parts by weight per 100 parts by weight of the base rubber. If desired, zinc oxide and barium sulfate may be blended in the rubber composition for specific gravity adjustment while antioxidants may also be blended.

[0014] The intermediate layer 2 has a radial thickness of at least 1 mm, preferably at least 1.3 mm, a specific gravity of less than 1.2, preferably 0.9 to 1.19, and a hardness of less than 80, preferably 45 to 75 on JIS C scale. With a thickness of less than 1 mm, repulsion is lowered to reduce flying distance. With a specific gravity of 1.2 or more, the ball has a heavier weight which exceeds the weight requirement of golf balls. With a JIS C scale hardness of 80 or higher, feeling becomes poor.

[0015] The intermediate layer 2 can be effective in compensating for lower repulsion of the center core 1 which is made soft. It is formed of a soft (JIS C scale hardness < 80), repulsive thermoplastic polyester elastomer.

[0016] The thermoplastic polyester elastomers are polyether ester multi-block copolymers e.g. as may be synthesized from terephthalic acid, 1,4-butane diol, and polytetramethylene glycol (PTMG) or polypropylene glycol (PPG) so that the polybutylene terephthalate (PBT) portion forms hard segments and the polytetramethylene glycol (PTGM) or polypropylene glycol (PPG) forms soft segments. For example, Hytrel® 4047 and G3548W are commercially available from Toray-duPont K.K.

[0017] Examples of the ionomer resin which can be mixed with the thermoplastic elastomer include relatively high repulsion Himilan® 1605 and 1707 commercially available from Mitsui-duPont Polychemical K.K. Usually 0 to 50 parts by weight of the ionomer resin is mixed with 100 parts by weight of the thermoplastic elastomer.

[0018] In addition to the thermoplastic elastomer (and/or ionomer resin) the composition of which the intermediate layer is formed may further contain weight control agents, for example, inorganic fillers such as zinc oxide and barium sulfate, coloring agents such as titanium dioxide, and other additives.

The cover 3 has a radial thickness of 1 to 3 mm, preferably 1.5 to 2.5 mm. A cover of more than 3 mm thick is low in repulsion and feeling whereas a cover of less than 1 mm thick is low in durability such as cut resistance. The hardness of the cover 3 is 85 or higher, more preferably 85 to 100 on JIS C scale. A cover with a hardness of less than 85 would be less repulsive.

[0019] The cover 3 may be formed of an ionomer resin which is conventionally used as the cover of solid golf balls. Exemplary ionomer resins are Himilan® 1706 and 1605 commercially available from Mitsui-duPont Polychemical K.K.

EXAMPLE

[0020] Examples of the present invention are given below by way of illustration and not by way of limitation.

Examples and Comparative Examples

[0021] Using a center core, intermediate layer, and cover having the composition shown in Table 1, three-piece solid golf balls (Examples 1-7, Comparative Examples 1-2) and two-piece solid golf balls (Comparative Examples 3-4) were prepared which had the parameters and test properties shown in Table 2.

[0022] The center core and the core of the two-piece ball were prepared by kneading the respective components in a roll mill and pressure molding at 155 °C for 15 minutes. The intermediate layer was formed by injection molding so as to enclose the outer surface of the center core. The cover was formed around the intermediate layer or the outer surface of the two-piece ball core by injection molding. The solid golf balls were completed in this way.

[0023] The golf balls were evaluated for flying performance, feeling, and durability by the following tests.

Flying performance

[0024] Using a swing robot manufactured by True Temper Co., the ball was hit by a driver at a head speed of 45 m/s and 35 m/s (abbreviated as HS45 and HS35 in Table 2, respectively) to measure the flying distance.

Feeling

[0025] Professional golfers evaluated a feeling on impact according to the following criterion.

○: good
△: average
X: Poor

Durability

[0026] Using a flywheel hitting machine, the ball was repeatedly hit at a head speed of 38 m/s until the ball was broken. With the number of hits counted, the ball was rated according to the following criterion.

○: good
△: average
X: poor

Table 1

	Example							Comparative Example			
	1	2	3	4	5	6	7	1	2	3	4
Center core											
Cis-1,4-polybutadiene	100	100	100	100	100	100	100	100	100	100	100
Zinc acrylate	25	25	15	25	25	25	25	25	25	15	
Zinc oxide	52	34	37	26		25	25	75	33	29	
Antioxidant	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	
Dicumyl peroxide	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65	
Intermediate layer											
Hytrel 4047	100	100	100	100	100		80	100			
Hytrel G3548 W						100					
Himilan 1605							20				
Himilan 1650									50		
Surlyn 8120									50		
Cover											
Himilan 1706	50	50	50	50	50	50	50	50	50	50	50
Himilan 1605	50	50	50	50	50	50	50	50	50	50	50
Note: The amount of components blended are parts by weight and their proportion is independent among the center core, intermediate layer, and cover.											

Table 2

	Example							Comparative Example			
	1	2	3	4	5	6	7	1	2	3	4
Center core											
Outer diameter, mm	27.68	31.52	31.57	35.24	36.40	31.56	31.56	23.80	31.57	38.58	38.60
Hardness, JIS C	73	73	53	73	73	73	73	73	73	53	81
Specific gravity	1.32	1.25	1.24	1.19	1.03	1.18	1.18	1.46	1.35	1.18	1.16
Intermediate layer											
Thickenss, mm	5.3	3.5	3.5	1.8	1.8	3.5	3.4	7.1	3.5		
Hardness, JIS C	61	61	61	61	61	50	68	61	82		
Specific gravity	1.10	1.10	1.10	1.10	1.10	1.18	1.18	1.10	0.97		
Cover											
Thickness, mm	2.2	2.1	2.1	1.9	2.0	2.1	2.2	2.4	2.1	2.0	2.0
Hardness, JIS C	91	91	91	89	91	91	91	91	91	91	89
Sepcific gravity	0.95	0.95	0.95	0.98	0.95	0.95	0.95	0.95	0.95	0.95	0.98
Performance											
W1 HS45 carry, m	208.0	209.0	209.0	210.5	210.0	209.0	210.0	205.0	209.0	208.0	210.0
total, m	220.5	220.0	221.5	222.5	220.0	221.0	222.0	218.0	221.0	220.0	220.0
W1 HS35 carry, m	141.0	141.0	142.0	141.0	142.0	142.5	141.5	139.0	141.0	141.0	139.5
total, m	147.5	148.0	148.5	148.0	148.5	149.0	148.5	145.0	148.0	148.0	145.5
Feeling	○	○	○	○	○	○	○	○	×	○	×
Durability	○	○	○	○	○	○	○	○	○	×	○

[0027] As is evident from Table 2, the three-piece solid golf balls, and particularly those with the preferred selected dimensions and densities etc. of their components, had a good balance of properties in that the center core can be made soft so as to ensure a pleasant feeling without deteriorating flying performance and durability.

[0028] There has been described a three-piece solid golf ball which includes a core, intermediate layer and cover having controlled size, hardness and specific gravity so that the ball has a good total balance of properties in that a relatively soft center core is used to ensure a pleasant feeling at no sacrifice of flying performance and durability.

[0029] Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Claims

1. A three-piece solid golf ball comprising a centre core (1), an intermediate layer (2) around the core and a cover (3) enclosing the intermediate layer and core;

   the centre core (1) having a diameter of at least 26 mm and a specific gravity less than 1.4;
   the intermediate layer (2) being mainly of thermoplastic polyester elastomer, having a thickness of at least 1 mm, a specific gravity less than 1.2 and a hardness less than 80 on the JIS C scale, and
   the cover having a thickness in the range 1 to 3 mm and a hardness of at least 85 on the JIS C scale.

2. A golf ball according to claim 1 wherein the centre core (1) has a hardness of not more than 80 (JIS C).

3. A golf ball according to claim 2 in which the centre core (1) has a diameter in the range 27 to 37 mm, a specific gravity in the range 1 to 1.35 and hardness in the range 40 to 75 (JIS C);

   the intermediate layer (2) is at least 1.3 mm thick, has a specific gravity in the range 0.9 to 1.19 and hardness in the range 45 to 75 (JIS C), and
   the cover (3) has a thickness in the range 1.5 to 2.5 mm and hardness in the range 85 to 100 (JIS C).

4. A golf ball according to any one of the preceding claims wherein the centre core (1) is of a polybutadiene-based rubber composition.

Patentansprüche

1. Dreiteiliger massiver Golfball, umfassend einen zentralen Kern (1), eine Zwischenschicht (2) um den Kern und eine Hülle (3), die die Zwischenschicht und den Kern umschließt;

   wobei der zentrale Kern (1) einen Durchmesser von zumindest 26 mm und ein spezifisches Gewicht unter 1,4 aufweist;

   die Zwischenschicht (2) hauptsächlich aus thermoplastischem Polyesterelastomer besteht, eine Dicke von zumindest 1 mm, ein spezifisches Gewicht von weniger als 1,2 und eine Härte unter 80 auf der JIS C-Skala aufweist, und

   die Hülle eine Dicke im Bereich von 1 bis 3 mm und eine Härte von zumindest 85 auf der JIS C-Skala aufweist.

2. Golfball nach Anspruch 1, worin der zentrale Kern (1) eine Härte nicht über 80 (JIS C) aufweist.

3. Golfball nach Anspruch 2, bei dem der zentrale Kern (1) einen Durchmesser im Bereich von 27 bis 37 mm, ein spezifisches Gewicht im Bereich von 1 bis 1,35 und eine Härte im Bereich von 40 bis 75 (JIS C) aufweist;

   die Zwischenschicht (2) eine Dicke von zumindest 1,3 mm, ein spezifisches Gewicht im Bereich von 0,9 bis 1,19 und eine Härte im Bereich von 45 bis 75 (JIS C) aufweist, und

   die Hülle (3) eine Dicke im Bereich von 1,5 bis 2,5 mm und eine Härte im Bereich von 85 bis 100 (JIS C) aufweist.

4. Golfball nach einem der vorangegangenen Ansprüche, worin der zentrale Kern (1) aus einer Kautschukzusammensetzung auf Polybutadienbasis besteht.

Revendications

1. Balle de golf pleine en trois morceaux, comprenant un noyau central (1), une couche intermédiaire (2) autour du noyau et un couvercle (3) enfermant la couche intermédiaire et le noyau.

   le noyau central (1) ayant un diamètre d'au moins 26 mm et une densité de moins de 1,4 ;
   la couche intermédiaire (2) étant principalement en un polyester élastomère thermoplastique ayant une épaisseur d'au moins 1 mm, une densité de moins de 1,2 et une dureté de moins de 80 à l'échelle JIS C et
   le recouvrement ayant une épaisseur dans la gamme de 1 à 3 mm et d'une dureté d'au moins 85 à l'échelle JIS C.

2. Balle de golf selon la revendication 1, où le noyau central (1) a une dureté de pas plus de 80 (JIS C).

3. Balle de golf selon la revendication 2, dans laquelle le noyau central (1) a un diamètre de l'ordre de 27 à 37 mm, une densité de l'ordre de 1 à 1,35 et une dureté de l'ordre de 40 à 75 (JIS C) ;

   la couche intermédiaire (2) a au moins 1,3 mm d'épaisseur, a une densité de l'ordre de 0,9 à 1,19 et une dureté de l'ordre 45 à 75 (JIS C), et
   le recouvrement (3) a une épaisseur de l'ordre de 1,5 à 2,5 mm et une dureté de l'ordre de 85 à 100 (JIS C).

4. Balle de golf selon l'une quelconque des revendications précédentes où le noyau central (1) est une composition de caoutchouc à base de polybutadiène.